Supporting information

Product Protection, the Key to Developing High Performance Methane Selective Oxidation Catalysts

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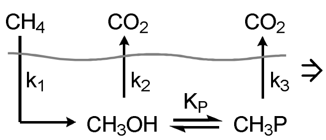
S.1. Kinetic Analysis

Kinetic model for the irreversible oxidation of CH_4, CH_3OH, and CH_3P (a protected form of methanol, e.g. $CH_3OH_2^+$ or CH_3OSO_3H) in a batch process with constant acidity and the methane pressure P_{CH4} held constant:



$\Rightarrow$ $k_{ox} = k_2/(1+K_P) + k_3K_P/(1+K_P)$

$[prod](t) = [CH_3OH] + [CH_3P]$
$= (k_1P_{CH4}/k_{ox})[1\text{-}exp(\text{-}k_{ox}t)]$

$S(t) = (1 - exp(-k_{ox}t)) / k_{ox}t$

Setup:

[prod] = [CH3OH] + [CH3P]

K_P = [CH3P]/[CH3OH]

[prod] = [CH3OH](1 + K_P)

$$d[prod]/dt = k_1P_{CH4} - k_2[CH3OH] - k_3[CH3P]$$

$$= k_1P_{CH4} - [prod]\{k_2/(1+K_P) + k_3K_P/(1+K_P)\} \qquad k_{ox} \equiv \{k_2/(1+K_P) + k_3K_P/(1+K_P)\}$$

$$= k_1P_{CH4} - [prod]\{k_{ox}\}$$

$$d[CO2]/dt = k_2[CH3OH] + k_3[CH3P]$$

$$= k_{ox}[prod]$$

$$S(t) = [prod] / \{[prod] + [CO2]\}$$

Solution:

$$[prod] = (k_1P_{CH4}/k_{ox})(1 - e^{-koxt})$$

$$[CO2] = k_1P_{CH4}\,(t - (1 - e^{-koxt})/k_{ox})$$

$$S = (1 - e^{-koxt}) / k_{ox}t$$

This model ignores changes in rates and the protection equilibrium constant which result from the increase in pH as the reaction proceeds.

Estimating kinetic parameters:

Values of k_1P_{CH4} and k_{ox} describing the Catalytica system are estimated (using a different kinetic model acknowledging the decay of methane pressure) as follows from the observations reported in Science, v280 p560 1998: “The reaction of methane (3400 kPa, 115mmol) with 80 ml of 102% H_2SO_4 containing a 50 mM concentration of ((bpym)$PtCl_2$) at 220°C for 2.5 hours resulted in ~90% methane conversion and the formation of ~1 M solutions of methyl bisulfate at 81% selectivity.”

Assuming 1st order decay of the methane pressure, and 90% conversion after 9000s:

$P_{CH4} = P_{CH4}^0 \exp(-kt)$

$3.4[\text{atm}] = 34[\text{atm}]\cdot\exp(-k[s^{-1}]\cdot 9000[s])$

$k = 2.6E\text{-}4\ s^{-1}$

Or equivalently, in terms of molarity of product generated:

$M_{prod} = M_{prod}^0(1-\exp(-kt))$

where M_{prod}^0 = .115moles/.08L = 1.4M represents the concentration of product if all methane became product with 100% selectivity (essentially this converts units from atmospheres-methane-per-second to molarity-product-per-second.) We estimate k_1P_{CH4} (in molarity-product-per-second), appropriate for 34 atm methane and 0.08L of 50mM catalyst, from the initial rate at 34 atm methane:

$d(M_{prod})/dt = M_{prod}^0\cdot k\cdot\exp(-kt)$

$d(M_{prod})/dt|_{t=0} = (1.4[M])(2.6E\text{-}4[s^{-1}])(1)$ = **$3.7E\text{-}4[M\cdot s^{-1}]$? k_1P_{CH4}**

The aggregate rate of oxidation k_{ox} is estimated from the reported selectivity. Assuming the rate of CO2 generated per liter solution is proportional to the product concentration [prod] and that product concentration increases exponentially as above (neglecting the slow oxidation of product to CO2),

$d[CO_2]/dt \quad = k_{ox}M_{prod} = k_{ox}M_{prod}^0(1 - \exp(-kt))$

$d[CO2] \quad = k_{ox}M_{prod}^0(1 - \exp(-kt))\, dt$

$[CO2]|_0^{[CO2]} \quad = k_{ox}M_{prod}^0(t + \exp(-kt)/k)\ |_0^t$

Substituting

$[CO2]_{t=9000}$ = (.115M)(0.19)(0.90)/(0.08L)

M_{prod}^0 = (.115mol)/(0.08L)

$k = 2.6E\text{-}4s^{-1}$

leads to k_{ox} **= 3.3E-5 [s^{-1}]**. We take these values of k_1P_{CH4} and k_{ox} to be appropriate for 100% H_2SO_4.

To estimate k_2 and k_3 separately, we first take K_P from the calculated free energy of

CH_3OH(1mM) + $2H_2SO_4$(l)→ CH_3OSO_3H(1mM) + HSO_4^- (**1**M) + H_3O^+(**1**M) ΔG = -14.2 kcal/mol

or K_P **= 2E6** at 220C. 1 molar H_3O^+ corresponds to 99% H_2SO_4 by mass. To estimate ΔG appropriate for 100% H_2SO_4, we employed the vapor pressures of H_2SO_4 and H_2O over 99% and 100% H_2SO_4 at 200°C reported in Perry's Chemical Engineers' Handbook (McGraw-Hill Professional; 7th ed, 1997, p2-78). (H_2O: 0.00352 bar over 99%, 0.0003 bar over 100%; H_2SO_4: 0.00505 bar over 99%, 0.00538 bar over 100%) Assuming each molecule of gaseous H_2O dissolved in concentrated H_2SO_4 generates one $H3O^+$ and one $HSO4^-$, the bisulfate and hydronium products of the esterification equilibrium are 2.2 kcal/mol more stable in 100% H_2SO_4 than in 99%. $\Delta G|_{100\%}$ is then -16.4 kcal/mol, or K_P **= 2E7**.

Assuming that methane oxidation is proton-catalyzed, we also used this change in proton chemical potential with acid concentration to correct k_1P_{CH4} for 99% H_2SO_4. With a free energy barrier 2.2 kcal/mol higher in 99% H_2SO_4, this rate would (by transition state theory) decrease to $\mathbf{k_1P_{CH4}}$ = **3.5E-5[M·s^{-1}].**

The ratio of the rate of oxidation of CH_3OH to that of CH_3OSO_3H is k_2/k_3. This ratio is calculated based on the activation free energies given in Figure 2 for CH_3OSO_3H (41.5 kcal/mol) and in Figure 3 for CH_3OH (27.2 kcal/mol). Since $k_2 = k_3 x2E6$, K_P = 2E7 and $k_{ox} = k_2/(1+K_P) + k_3K_P/(1+K_P)$ = 3.3E-5, $\mathbf{k_2}$ **= 60 [s^{-1}]** and $\mathbf{k_3}$ **= 3E-5 [s^{-1}]**.

In summary, the curves in Figure 4 employ the following constants:

Table S.1.

	k_1P_{CH4} (Ms^{-1})	k_2 (s^{-1})	k_3 (s^{-1})	K_P
"KP = 0"	3.7E-4	60	3E-5	0
"99 %"	3.5E-5	60	3E-5	2E6
"100 %"	3.7E-4	60	3E-5	2E7
"KP→∞"	3.7E-4	60	3E-5	1E10

S.2. Computational Details

All calculations were performed with the hybrid density functional B3LYP.

Geometry optimizations included solvation using the Poisson-Boltzmann reactive field (PBF) with a dielectric constant of 98.0 and a probe radius of 2.205 to simulate sulfuric acid. For solvation of smaller ions two explicit solvent molecules were included.

For geometry optimizations the smaller LACVP** basis set augmented with an extra d-function on sulfur. For single point energies we used the LACV3P**++ basis set augmented with one f-function on platinum and two d-functions and an f-function on sulfur. Frequency calculations were performed numerically including the PBF-solver at the B3LYP/LACVP**(+d on S) level.

Free energies were calculated as the sum G = E(lacv3p**++ 2df(S) f(Pt)) + Gsolv + ZPE + ΔH(500). For gas phase molecules an empirical correction of 0.4*Strans/rot was added to account for the higher translational and rotational entropy in the gas phase compared to the solution phase.

All species are calculated at 1 M or 1 atm except sulfuric acid, which is corrected to 18 M to reflect typical experimental conditions.

S.3 *Solvation of ions*

We found that simple solvation of small ions by the PBF method did not yield good results. Inclusion of one solvent molecule improved the result, and further improvement was found when two explicit solvent molecules were used to solvate the ions. The large metal complexes are not affected substantially by inclusion of explicit solvent. See supporting info of M. Ahlquist, R. A. Periana, W. A. Goddard III *Chem. Commun.* **2009**, 2373, available online at www.rsc.org **DOI:** 10.1039/b821854d

S.4. More details on the mechanisms

A mechanism with low barriers for oxidation of 16 was found. It is outlined in figure S1.

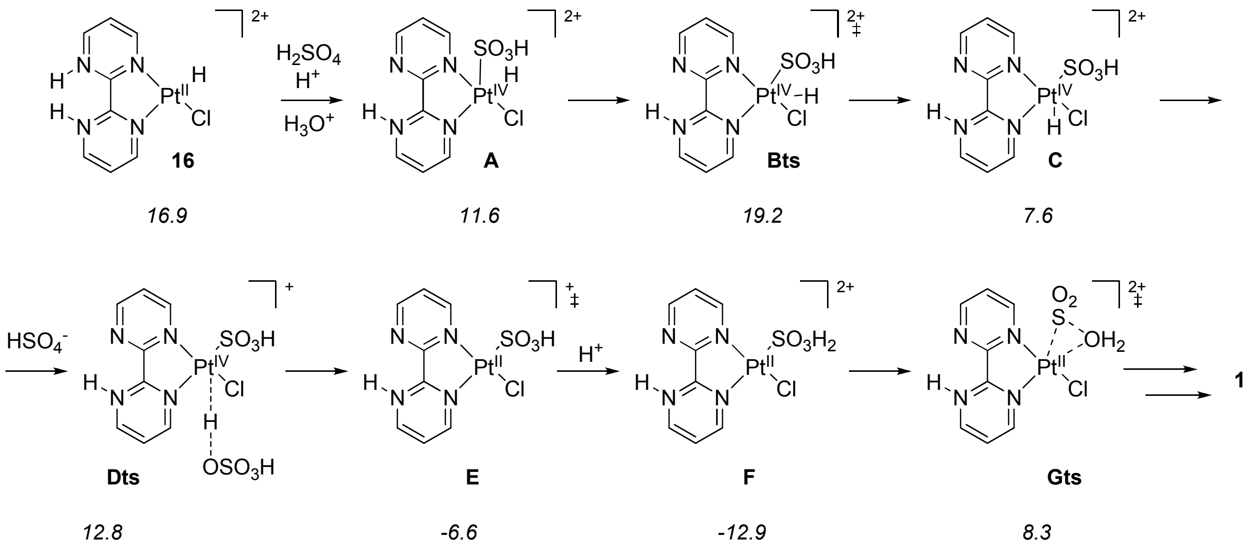
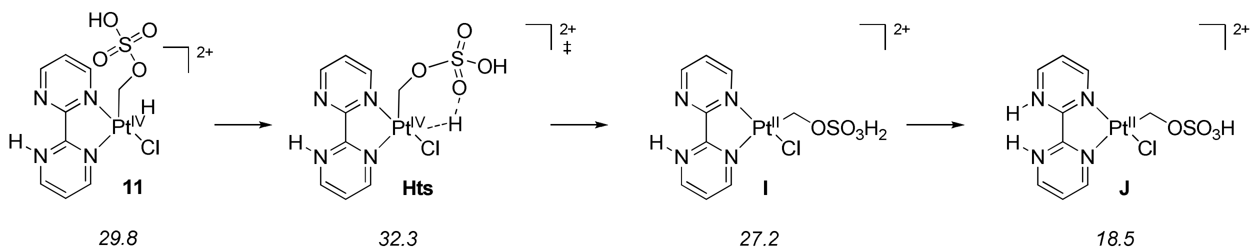


Figure S1. Oxidation of intermediate 16 by sulfuric acid.



Formation of the alkyl intermediate X in the reaction between 1 and methyl bisulfate was found be facile.

S.5. Cartesian coordinates and energies of complexes calculated.

1

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1807.23878632258

G_{solv} = -0.1684679

Pt1	−0.1974369198	0.2757412902	−0.2018467890
N2	1.8149185420	−0.0793723654	−0.0878986165
N3	0.4720619054	2.1930001671	−0.2083019236
C4	1.8237941322	2.3178918411	−0.1430888947
C5	2.5454986094	1.0420355722	−0.0819183316
N6	3.8825086323	0.9934432813	−0.0162389598
N7	2.4980497822	3.4495897670	−0.1268493935
C8	−0.2482907674	3.3317881494	−0.2608886718
C9	1.7858397917	4.5857814134	−0.1797703831
C10	2.4359201368	−1.2773304257	−0.0299980666
C11	4.5504154849	−0.1753375411	0.0470223301
C12	3.8221237328	−1.3568620050	0.0394205014
C13	0.3930061809	4.5666732510	−0.2482295606
H14	1.7995140044	−2.1555537472	−0.0391498804
H15	5.6321868176	−0.1243776487	0.1005021898
H16	−1.3263202240	3.2354298684	−0.3120555149
H17	2.3426173884	5.5184736336	−0.1658487137
H18	−0.1862852376	5.4824533424	−0.2899894666
H19	4.3190285152	−2.3191103760	0.0882172824
Cl20	−2.4912849371	0.8436486761	−0.3335714729
H21	4.3894422856	1.8850042908	−0.0142130799
S22	−1.7153950780	−2.5232219134	0.3829250299
O23	−1.9413901940	−2.0676569257	1.7329840333
O24	−1.4952039666	−3.9279770933	0.1660802259
O25	−0.5769226230	−1.7536417548	−0.2830484880
O26	−3.0012653484	−2.1875317190	−0.4946596888

H27	-3.1790230149	-1.2211466413	-0.4710131390

2ts

$E_{lacv3p^{**}++(+ 2df\ on\ S,\ f\ on\ Pt)}$ = -1848.00880194501

G_{solv} = -0.2931775

O3	0.1485734484	0.0914126995	-0.1114364620
Pt1	-0.1109954319	-0.0263165229	2.6197599415
H22	1.7846153738	-0.0608479291	1.6082307563
C21	2.8413355552	-0.0558954701	1.9583811043
N2	-1.3663377661	-0.0836470808	4.1865470967
N3	-0.3204339947	-2.0804167776	2.8135646591
Cl4	0.0819595569	2.3003908891	2.5230459547
C5	-1.7080921339	-1.3276466324	4.6165027297
C6	-1.1191637422	-2.4173035560	3.8349779305
N7	-2.4862165306	-1.5941650535	5.6429994855
C8	-2.9844914272	-0.5527701077	6.3275493076
C9	-2.6925242451	0.7610778211	5.9613729336
C10	-1.8643414681	0.9722656753	4.8623468586
N11	-1.3668738437	-3.6977542429	4.1349618991
C12	-0.8290495296	-4.7097777433	3.4282245383
C13	0.0039181768	-4.4006200405	2.3614434290
C14	0.2453213538	-3.0610073546	2.0711696262
H15	-3.6214187542	-0.7807168491	7.1781735119
H16	-3.0890888828	1.6086428912	6.5098564312
H17	-1.5860130466	1.9609230321	4.5203928798
H18	-1.0783606013	-5.7185841834	3.7394483417
H19	0.4569744593	-5.1877098826	1.7691047949
H20	0.9058806463	-2.7706946385	1.2567679048
H23	2.9116383141	-0.3854533163	2.9931649531
H24	3.3828971062	-0.7375600776	1.3000406377
H25	3.1983605846	0.9700619367	1.8544937213

H26	−1.9843017009	−3.8896434077	4.9324376779
S5	0.8495214594	−0.6669416360	−1.1108796337
O6	2.0228236398	0.1822398960	−1.7089330776
O7	−0.1681440536	−0.8242178886	−2.2850692891
O8	1.4231498649	−1.9214117734	−0.7351397817
H32	1.7466752138	1.0879263803	−1.9616498509
H33	0.1689195079	−1.4043143693	−2.9968227706

3

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1147.57978191764

G_{solv} = -0.3013535

Pt1	−0.0198781279	−0.0289158607	0.0106850468
N2	−0.0273205197	−0.0249337819	2.0340019871
N3	2.0172610361	0.0248868729	0.3555717119
Cl4	−2.3567540888	−0.0846001515	−0.2261507526
C5	1.2020819823	−0.0002658319	2.6110818859
C6	2.3175611017	0.0275577131	1.6595395655
N7	1.4437667996	0.0041616227	3.9040334320
C8	0.3826413457	−0.0160420883	4.7269880979
C9	−0.9200319757	−0.0362845146	4.2309975784
C10	−1.0996696604	−0.0410469521	2.8505838708
N11	3.5878609406	0.0592664841	2.0804366069
C12	4.6233309507	0.0898272824	1.2200986894
C13	4.3508407731	0.0874103590	−0.1407659401
C14	3.0221390402	0.0522954578	−0.5474649665
H15	0.5862002635	−0.0147780301	5.7940919014
H16	−1.7796549771	−0.0488906296	4.8921288270
H17	−2.0787712369	−0.0582721560	2.3876809349
H18	5.6208926668	0.1134376991	1.6446294759
H19	5.1519852034	0.1120784544	−0.8706646886
H20	2.7540621349	0.0456423055	−1.5980591755

C21	0.0202406377	0.3165211670	-2.4559616852
H22	0.0833356218	-0.6032756383	-1.7729426578
H23	0.0694897574	1.3192373098	-2.0241532925
H24	0.8796120590	0.1633869867	-3.1116701133
H25	-0.9337600798	0.1890866232	-2.9670688304
H26	3.7496242085	0.0589475887	3.0940480819

4ts

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = --1147.56326505772

G_{solv} = -0.3012988

C1	0.0000000000	0.0000000000	0.0000000000
H2	0.0000000000	0.0000000000	1.6923738592
Pt4	1.5440267323	0.0000000000	1.5261773486
N9	3.5247932370	-0.1741232618	2.3926982876
N10	1.7428629243	-2.0554676899	1.6249472919
N11	5.0423226413	-1.7839390953	3.1099282797
N12	3.2567664292	-3.7589040253	2.3116865276
Cl13	1.5378410495	2.3493645923	1.5330677707
C14	3.8599476171	-1.4500308037	2.5755815053
C15	2.9105142663	-2.4974582508	2.1565751038
C16	5.9449962802	-0.8513447060	3.4739795981
C17	5.6356841775	0.4870274287	3.2798447544
C18	4.3961736146	0.7983412550	2.7276469096
C19	2.3814724951	-4.6928065926	1.9066541779
C20	1.1553990059	-4.3414888961	1.3446232693
C21	0.8597421663	-2.9872171670	1.2192817911
H22	6.8760652878	-1.2084905575	3.9001684245
H23	6.3395253167	1.2663909399	3.5483005546
H24	4.0822313243	1.8211089307	2.5415637686
H25	2.6741581368	-5.7303862293	2.0386056550
H26	0.4450308778	-5.0903997469	1.0118425626

H27	−0.0776562804	−2.6464845174	0.7953954737
H28	0.5555113146	−0.5919469927	−0.7297053313
H29	−0.9711992805	−0.4528546129	0.2088790124
H30	−0.1029551089	1.0418304656	−0.2920864959
H32	5.2435334059	−2.7826919864	3.2306755407

5

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1147.56014308343

G_{solv} = -0.3169348

Pt4	−0.0124361444	−0.0004466131	−0.0400920562
H2	0.1674508145	0.0863152595	1.4580980345
N9	2.3317727725	0.0198439682	−0.0148842934
N10	0.4765883703	−2.0280379919	0.0782432136
N11	4.0756031240	−1.5041452062	0.2233265423
N12	2.2846047348	−3.5652653368	0.2153372754
Cl13	−0.3311635330	2.3332573225	0.0763486157
C14	2.7664693346	−1.2271966328	0.0881354871
C15	1.7949989517	−2.3435147593	0.1128148127
C16	5.0002934421	−0.5274182149	0.2878213903
C17	4.5780090350	0.7929501205	0.2244550917
C18	3.2146398679	1.0327934340	0.0651573221
C19	1.4139959852	−4.5809691472	0.3081590717
C20	0.0396408676	−4.3551768595	0.3168096997
C21	−0.4022836180	−3.0423560776	0.1964323252
H22	6.0357553857	−0.8325136535	0.3946726726
H23	5.2888990190	1.6080451731	0.2974316712
H24	2.8105688276	2.0398996042	0.0176630763
H25	1.8296629960	−5.5818726247	0.3847105196
H26	−0.6722511588	−5.1668802887	0.4172010478
H27	−1.4573847083	−2.7977310343	0.1991870040
H32	4.3462986141	−2.4915442858	0.2886476711

C1	−1.9947856780	−0.2783028679	0.5284566923
H28	−2.5128171693	−0.7241960690	−0.3239297159
H29	−1.9896606707	−0.9470074391	1.3939488892
H30	−2.4221057690	0.6851088248	0.8051960088

6

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1147.53992921979

G_{solv} = -0.3428968

Pt1	−0.2144374643	0.0796851473	−0.2527294363
N2	1.8167441063	−0.1313275804	−0.0533134413
N3	0.4802438879	2.1722295315	−0.1381113628
C4	−0.6404977752	−1.9262119732	−0.3588346720
C5	1.8022245258	2.2759506107	−0.0172910840
C6	2.5432073116	1.0006051144	0.0339457754
N7	3.8837944649	0.9419760389	0.1645486034
N8	2.3945187564	3.4866955643	0.0533540382
C9	−0.2719423291	3.2916329720	−0.1881002364
C10	1.6822365347	4.6292399045	0.0065623267
C11	2.4682188390	−1.3222454176	−0.0015704451
C12	4.5602608815	−0.2183720595	0.2179262699
C13	3.8435844544	−1.4036298461	0.1353397256
C14	0.3020821136	4.5547955008	−0.1170977286
H15	1.8580972186	−2.2138817437	−0.0729922231
H16	5.6374800934	−0.1551829589	0.3226285823
H17	−1.3436265359	3.1452446148	−0.2860855880
H18	2.2410980318	5.5563021145	0.0692017344
H19	−0.3024430244	5.4537548333	−0.1562978072
H20	4.3415556878	−2.3655982024	0.1739238382
H21	−1.7108936897	−2.0977218772	−0.4985537849
H22	−0.3212922466	−2.4119714328	0.5721497045
H23	−0.0980890180	−2.3637605996	−1.2067487605

Cl24	−2.4967352898	0.5779710188	−0.4704737891
H25	4.4376744707	1.7965560283	0.2273694252
H26	3.4063443089	3.5814954766	0.1447340856

7

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1846.80607318972

G_{solv} = -0.2974632

Pt1	0.0847946036	0.3031861885	0.5353460450
N2	1.9535724793	−0.1214242635	−0.2300941034
N3	0.5961813699	2.1441964666	−0.1149353788
C4	1.7883678416	2.2078295065	−0.7671848614
C5	2.5314530022	0.9452541886	−0.7953860864
N6	3.7340244529	0.8557006703	−1.3772350747
N7	2.2832210138	3.2669930742	−1.3708193995
C8	−0.1504270540	3.2684208528	−0.0875340347
C9	1.5427498860	4.3860547977	−1.3552508330
C10	2.6063108836	−1.3050712256	−0.2359817895
C11	4.4204759687	−0.3020267445	−1.4179625321
C12	3.8559126641	−1.4275432082	−0.8322934308
C13	0.3044897581	4.4243582816	−0.7153683758
H14	2.1131910220	−2.1434896301	0.2447660648
H15	5.3858302680	−0.2869574255	−1.9111694617
H16	−1.1061867094	3.2158448703	0.4187939564
H17	1.9488202861	5.2531686900	−1.8681212100
H18	−0.3033324028	5.3225735519	−0.7067929286
H19	4.3728985760	−2.3801621019	−0.8397633839
Cl20	−2.0275493130	0.9499221306	1.3249186282
H21	4.1194092944	1.7073572882	−1.8007568547
S22	−1.5605874019	−2.5638417840	0.5756353238
O23	−2.7428647610	−2.2541581493	1.2974832742
O24	−1.0476708155	−4.0173352121	0.8082217962

O25	−0.3255275729	−1.7931468237	0.8405751735
O26	−1.9224506823	−2.4834686081	−0.9419600311
H28	−1.7820582155	−4.6501564281	0.9658458272
C28	−1.0316108108	−3.0368980790	−1.9820006337
H29	−1.5501772747	−2.8199939216	−2.9151720716
H30	−0.0692426209	−2.5261385491	−1.9482165884
H31	−0.9258169558	−4.1112466323	−1.8336374336

8ts

$E_{lacv3p{*}{*}{+}{+}(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1846.77331606668

G_{solv} = -0.2942432

H30	0.0000000000	0.0000000000	0.0000000000
Pt1	0.0000000000	0.0000000000	1.9681108259
O25	2.4788956861	0.0000000000	0.3082591556
N2	1.1197269775	1.7386732872	2.4072941023
N3	−0.4020672770	0.1747819283	3.9405507948
C4	0.1679675294	1.2406628134	4.5587578214
C5	1.0029561502	2.0760186446	3.6969028817
N6	1.6418831300	3.1432369436	4.2095892858
N7	0.0425703192	1.5649493447	5.8297348273
C8	−1.1724694365	−0.6389343759	4.6949136869
C9	−0.7223458400	0.7667287325	6.5917523156
C10	1.9205750046	2.4898111496	1.6145724157
C11	2.4381655879	3.9308463594	3.4537618349
C12	2.5936742260	3.6064073095	2.1138346237
C13	−1.3511404494	−0.3580719474	6.0500002435
H14	2.0260481926	2.1584318895	0.5882203236
H15	2.9162254116	4.7740525497	3.9420039190
H16	−1.6219803865	−1.4891714687	4.1938770953
H17	−0.8254973869	1.0365347809	7.6388645096
H18	−1.9690483475	−1.0092429661	6.6593598690
H19	3.2292932815	4.2044594010	1.4701630660

Cl20	−1.2250144448	−1.9226251537	1.6825242415
H21	1.4912854976	3.3207511855	5.2096775353
S22	2.5984160134	−0.9843779399	−0.7421987288
O23	3.3444171754	−2.1768239776	−0.6069777328
O24	3.0384496674	−0.1573647151	−2.0131978439
O26	1.0917525212	−1.4286719622	−1.1014606631
H28	3.4548410887	−0.7351584076	−2.6819118958
C28	0.0815354343	−0.4525964382	−1.0549046745
H29	−0.8667913163	−0.9507167158	−1.2467178448
H31	0.2697843838	0.3976059819	−1.7170764480

9

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1846.77100860891

G_{solv} = -0.3048443

S1	5.5055875945	1.5338548385	0.8806282409
O2	5.3330023187	1.7511518530	2.2837998496
O4	6.4441440978	2.3136900645	0.1310272783
O5	4.1529862460	1.5723537349	0.1068024942
H6	3.3904571382	1.3320394808	0.6745586269
O6	5.8657347739	−0.0242091032	0.6268182847
C7	6.8919879048	−0.5877363497	1.4177107888
H8	6.8664526841	−1.6620801117	1.2613317152
H9	7.8946399578	−0.1731284924	1.0172371201
H10	6.8353834764	−0.3048628097	2.4685551731
Pt1	9.7355316442	−0.6013714279	1.0364383454
N2	11.7176379045	−0.9669159091	0.9641402367
N3	10.2593281261	0.6442582473	−0.5354715959
Cl4	9.2941770421	−2.0383330554	2.8368920666
C5	12.3963910587	−0.3044086316	−0.0060960901
C6	11.5655724409	0.5829843931	−0.8228758918
N7	13.6861772169	−0.4066813402	−0.2440653175
C8	14.3930094951	−1.2367818250	0.5390050119

C9	13.7849480718	−1.9595677752	1.5647599215
C10	12.4160633381	−1.8024305907	1.7597007114
N11	12.0990654652	1.3046377486	−1.8160380649
C12	11.3541712337	2.1276568567	−2.5774412402
C13	9.9955844403	2.2209590606	−2.3100639116
C14	9.4697671011	1.4597697889	−1.2710493650
H15	15.4572167213	−1.3201052901	0.3371635717
H16	14.3491991336	−2.6319781539	2.2014365100
H17	11.8710224538	−2.3304931104	2.5318365526
H18	11.8645273944	2.6754628652	−3.3617569129
H19	9.3596661645	2.8716069304	−2.8989409004
H20	8.4149348809	1.4938776730	−1.0182214426
H26	13.1075939753	1.2084647589	−1.9814958156

10ts

$E_{lacv3p**++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1846.7477473091

G_{solv} = -0.3045122

H31	0.0000000000	0.0000000000	0.0000000000
C7	0.0000000000	0.0000000000	1.5173325598
Pt1	1.5796934954	0.0000000000	−0.2473742701
H8	−0.9835310877	0.4413234624	1.3560035483
H10	−0.0287176172	−1.0574162137	1.7671787674
N2	3.6437364754	−0.0152719649	−0.7443422378
N3	1.9818921926	−2.0397278551	−0.1540998278
Cl4	1.3356321985	2.3196942882	−0.4450303490
C5	4.2061813162	−1.2411180635	−0.6765571636
C6	3.2700602691	−2.3357370737	−0.3756963054
N7	5.4861443215	−1.5215356860	−0.8232022288
C8	6.3106629718	−0.4836047347	−1.0406747365
C9	5.8337326829	0.8261476546	−1.1009884529
C10	4.4634071645	1.0314843562	−0.9510892795
N11	3.7097103671	−3.5991110225	−0.3118623988

C12	2.8929969037	-4.6303199295	-0.0251024706
C13	1.5493437701	-4.3637725081	0.1950971982
C14	1.1190490353	-3.0444750834	0.1174437417
H15	7.3667532200	-0.7105380198	-1.1580130903
H16	6.5043797792	1.6645235742	-1.2546732250
H17	4.0126128367	2.0178245815	-0.9820539730
H18	3.3376783550	-5.6181951861	0.0183863115
H19	0.8516310453	-5.1593136160	0.4282893775
H20	0.0774485734	-2.7827456151	0.2693475686
H26	4.7112991027	-3.7534924771	-0.4786254882
S1	1.9009586389	0.1685098590	3.3333343872
O2	1.8701710317	-1.2555110584	3.1951002914
O4	3.0454130087	0.9384851062	2.9794276368
O5	1.4776718277	0.6407688516	4.7567136553
H6	0.8563942870	0.0302136576	5.2075905258
O6	0.6340326240	0.7838406968	2.4653730004

11

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1846.78043775539

G_{solv} = -0.2941368

H1	0.0203782940	0.1056611787	-0.0400576894
C2	0.0980684255	-0.0601432284	2.4775068454
Pt3	1.3419521995	0.0419065578	0.7353456652
H4	-0.7266898585	-0.6959516684	2.1618401981
H5	0.7557147251	-0.5101904312	3.2204664296
N6	3.2254205753	-0.2531340756	1.9546960162
N7	1.4056263902	-2.0171635498	0.9421917429
Cl8	1.4476570252	2.3893801991	0.5970959476
C9	3.4771879701	-1.5486963208	2.0885783881
C10	2.5072578095	-2.5285933437	1.5494903452
N11	4.5631730659	-1.9790457397	2.7522342876
C12	5.4246125469	-1.1201115364	3.3316984726

C13	5.1703136738	0.2415209428	3.2422394517
C14	4.0460529141	0.6480011888	2.5284535044
N15	2.7457620841	-3.8099728071	1.7382713064
C16	1.8129163354	-4.6794375017	1.3188507399
C17	0.6221553260	-4.2480055991	0.7358263116
C18	0.4470456520	-2.8803783594	0.5499793120
H19	6.2772227288	-1.5493276767	3.8466168363
H20	5.8288643459	0.9628472255	3.7126067404
H21	3.7835060971	1.6944435280	2.4108621766
H22	2.0226880587	-5.7351341660	1.4668435664
H23	-0.1508773324	-4.9450680742	0.4327784403
H24	-0.4486064289	-2.4664896031	0.0990365013
S25	0.2415689369	1.9679371197	4.1406583631
O26	-0.6627453720	1.9084071301	5.2392708504
O27	1.5987762605	1.5269190655	4.2550162439
O28	0.1274540195	3.4151339287	3.5670160203
H29	0.7345226774	3.5664480677	2.8089910079
O30	-0.4515211271	1.1413202821	2.9022222787
H31	4.7105093276	-2.9905575783	2.8193904586

12

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1222.86254142258

G_{solv} = -0.294067

Pt1	-0.2148630652	0.1461600399	-0.1600573004
N2	1.8097376416	-0.1488671360	-0.1166140655
N3	0.4343591143	2.0715145489	-0.1426928167
C5	1.7708297741	2.2228386205	-0.1295868423
C6	2.5453176090	0.9715723513	-0.1074436563
N7	3.8869268001	0.9039697003	-0.0966515746
N8	2.3167576886	3.4483652779	-0.1619153940
C9	-0.3564807433	3.1704993830	-0.2078775090
C10	1.5708019972	4.5685215683	-0.2218860011

C11	2.4228036753	−1.3547460035	−0.1130635625
C12	4.5429224446	−0.2721900231	−0.0980732775
C13	3.8067252145	−1.4499529733	−0.1079197356
C14	0.1896647255	4.4458067805	−0.2509242103
H15	1.7766366085	−2.2265834828	−0.1134549420
H16	5.6265261664	−0.2270446539	−0.0901780720
H17	−1.4264872963	2.9971828021	−0.2324517186
H18	2.1045909075	5.5122420011	−0.2477042352
H19	−0.4471797287	5.3213525960	−0.3088608023
H20	4.2985810120	−2.4162797056	−0.1101599335
Cl36	−2.5120205356	0.6026412620	−0.2584604267
H37	4.4556349054	1.7533116121	−0.0872004295
O22	−0.6518362861	−1.8922759954	−0.3174252344
H23	−1.1956349022	−2.1955097352	0.4327626645
C24	−1.2216448643	−2.4005142563	−1.5744989637
H25	−0.4910416383	−2.1870960819	−2.3534828833
H26	−1.3536486895	−3.4771514437	−1.4581673955
H27	−2.1683484148	−1.9036711321	−1.7885234044
H28	3.3318546229	3.5672862426	−0.1423998837

13ts

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1222.81414914422

G_{solv} = -0.2925414

Pt1	0.0000000000	0.0000000000	0.0000000000
H25	0.0000000000	0.0000000000	2.0796099658
O22	2.0592196653	0.0000000000	1.8813565425
N2	0.9010857060	−1.8791525895	−0.3349133286
N3	−0.7044017222	−0.3792968778	−1.8369179097
C5	−0.3526779790	−1.5849444615	−2.3601275121
C6	0.5318259843	−2.3862947724	−1.5157480445
N7	0.9720077680	−3.5869533316	−1.9336410377
N8	−0.7201232250	−2.0621687974	−3.5309231983

C9	−1.5047884089	0.4106835651	−2.5870966267
C10	−1.5182886321	−1.2902939592	−4.2859193384
C11	1.7604951049	−2.5823413415	0.4398624333
C12	1.8097724402	−4.3395021898	−1.1856042018
C13	2.2294287111	−3.8347933660	0.0377800941
C14	−1.9319587738	−0.0316865599	−3.8395162104
H15	2.0643389606	−2.0931482214	1.3629586393
H16	2.1136356244	−5.2998102873	−1.5903584391
H17	−1.7813152672	1.3697241523	−2.1635169589
H18	−1.8212311617	−1.6890078574	−5.2499618216
H19	−2.5748964158	0.5998702848	−4.4438365675
H20	2.9103073184	−4.4009428997	0.6640869328
Cl36	−1.0165402421	2.0475683324	0.2084614679
H37	0.6377106731	−3.8975614515	−2.8535190844
H23	2.8273903420	0.5292566500	2.1438886123
C24	0.9001449340	0.4722071282	2.5757929979
H26	0.8377595903	0.1089488452	3.6090371601
H27	0.7855189908	1.5567113526	2.5367443258

14

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1222.81061689086

G_{solv} = -0.3062078

Pt1	−0.0082708144	−0.2716099943	0.0060654232
N2	0.0030492121	−0.1493376308	2.0502293913
N3	2.0180369598	−0.0583322728	0.3296244923
Cl4	−2.3316710338	−0.4999351394	−0.2195250134
C5	1.2253504888	0.0659931411	2.5952999274
C6	2.3243370747	0.1034076702	1.6237799027
N7	1.4784776957	0.2490787738	3.8746412308
C8	0.4298959131	0.2275061643	4.7130190831
C9	−0.8684085105	0.0161076783	4.2491544950
C10	−1.0554346887	−0.1748262725	2.8828110261

N11	3.5887879634	0.2961592226	2.0194549260
C12	4.6131363560	0.3335543079	1.1461830647
C13	4.3375012401	0.1530287584	-0.2020832106
C14	3.0158360945	-0.0477823720	-0.5825247680
H15	0.6385350885	0.3855113370	5.7671777172
H16	-1.7175669018	0.0034273566	4.9237675347
H17	-2.0305737967	-0.3428180047	2.4419476879
H18	5.6035509006	0.5024421184	1.5536733251
H19	5.1299161661	0.1685247795	-0.9414583851
H20	2.7448158933	-0.2065680994	-1.6204382698
C22	0.0410797790	0.4634493557	-2.6262987560
H23	0.0213314044	-0.4006686927	-1.7467477000
H24	0.7143237838	1.2602401978	-2.3083080576
H25	0.4788384058	-0.1849103176	-3.3910545745
H26	3.7546917238	0.4212710229	3.0243396358
O26	-1.2071435850	0.8527382379	-2.9824814361
H27	-1.4950310551	1.6063986160	-2.4405944653

15ts

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1222.80853465057

G_{solv} = -0.2984918

C1	0.0000000000	0.0000000000	0.0000000000
H2	0.0000000000	0.0000000000	1.7183603816
Pt3	1.4001635486	0.0000000000	2.4897329451
N4	3.3003046671	-0.1565981318	3.4910032445
N5	1.6055484757	-2.0355916706	2.5879256547
N6	4.9005643389	-1.7500890173	4.0704004976
N7	3.1446535229	-3.7400975589	3.2309002163
Cl8	1.3525444121	2.3539397546	2.4470940348
C9	3.6941885062	-1.4275873596	3.5800249318
C10	2.7759964816	-2.4787208259	3.1128282653
C11	5.7726672201	-0.8116244995	4.4860975738

C12	5.3987066735	0.5219827830	4.4054680426
C13	4.1371562605	0.8207255669	3.8965715309
C14	2.2834586925	-4.6738875614	2.8004403622
C15	1.0436436217	-4.3245845872	2.2648884644
C16	0.7299982880	-2.9731446796	2.1731660103
H17	6.7299898336	-1.1581607870	4.8601239839
H18	6.0736958666	1.3079393362	4.7235873306
H19	3.7797577816	1.8410254557	3.7956050699
H20	2.5946188253	-5.7106517473	2.8903962769
H21	0.3400456029	-5.0755779373	1.9228777011
H22	-0.2152785004	-2.6299277514	1.7701489502
H23	0.9227201102	-0.5307392007	-0.2063563425
H24	-0.9282337372	-0.5514042636	0.1445475075
H25	5.1438910425	-2.7457475071	4.1098154435
O26	-0.0414136565	1.2106672646	-0.4398907321
H27	-0.9364161768	1.6044322274	-0.3898645608

16

$E_{lacv3p^{**}++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1108.21171198054

G_{solv} = -0.349928

H2	0.0224056041	-0.0001703410	2.3479162412
Pt3	1.5030735084	-0.0102295108	2.7784033464
N4	3.5859845360	-0.2563021581	3.4129620976
N5	1.6351322585	-2.0213243802	3.0388995279
N6	5.1503139924	-1.8550272349	4.0518776564
N7	2.9850211641	-3.8343966933	3.6327994898
Cl8	1.5178881867	2.3184623861	2.5191186121
C9	3.9059979702	-1.5262909624	3.6495783911
C10	2.8238306479	-2.5105624797	3.4406879517
C11	6.1071603748	-0.9221365547	4.2280423224
C12	5.8020918113	0.4099173397	3.9885264809
C13	4.5095837787	0.7103635214	3.5759191128

C14	1.9940750975	-4.7219696897	3.4363044739
C15	0.7559552485	-4.2515851826	3.0200948038
C16	0.6070857274	-2.8879297935	2.8297066357
H17	7.0782295617	-1.2768322317	4.5545525733
H18	6.5476393326	1.1851658528	4.1212731713
H19	4.1847535246	1.7260020360	3.3674769100
H20	2.2262905042	-5.7649625491	3.6183896080
H21	-0.0718207883	-4.9300785316	2.8489426794
H22	-0.3321005966	-2.4550274412	2.5074144038
H25	5.4115368087	-2.8237205457	4.2376287273
H23	3.8831243829	-4.2100446994	3.9397932304